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Generation and origin of natural gas in Lower Palaeozoic shales from southern Sweden

Niels Hemmingsen Schovsbo and Arne Thorshøj Nielsen

The Lower Palaeozoic succession in Scandinavia includes several excellent marine source rocks notably the Alum Shale, the Dicellograptus shale and the Rastrites Shale that have been targets for shale gas exploration since 2008. We here report on samples of these source rocks from cored shallow scientific wells in southern Sweden. The samples contain both free and sorbed hydrocarbon gases with concentrations significantly above the background gas level. The gases consist of a mixture of thermogenic and bacterially derived gas. The latter likely derives from both carbonate reduction and methyl fermentation processes. The presence of both thermogenic and biogenic gas in the Lower Palaeozoic shales is in agreement with results from past and present exploration activities; thermogenic gas is a target in deeply buried, gas-mature shales in southernmost Sweden, Denmark and northern Poland, whereas biogenic gas is a target in shallow, immature-marginally mature shales in south central Sweden. We here document that biogenic gas signatures are present also in gas-mature shallow buried shales in Skåne in southernmost Sweden.

In south central Sweden (Västergötland, Östergötland, Närke and Öland, Fig. 1), shallow (present burial <150 m) immature to marginally mature bituminous shale has been known for decades to contain gas and is currently under exploration (see summary in Schultz *et al.* 2015). Since 2009, many deep (>800 m) exploration drillings in northern Poland (including the Lebork S-1 well, Lehr & Keeley 2016), the Vendsyssel-1 well in Denmark (Ferrand *et al.* 2016) and the A3-1, B2-1, C4-1 wells in Skåne in southernmost Sweden (Pool *et al.* 2012), have demonstrated that the Lower Palaeozoic shale succession contains gas also in these areas (Fig. 1). In Denmark and Skåne, the average gas content is 30 ft^3 gas per ton of rock in the organic-rich Alum Shale Formation (Pool *et al.* 2012; Ferrand *et al.* 2016). The equivalent shale formation in northern Poland contains up to 268 ft^3 gas per ton of rock in the Lebork S-1 well (Lehr & Keeley 2016), which is comparable to the content within the core area of North American shale gas-producing formations (e.g. Jarvie 2012).

In this study, we present empirical data on the composition and isotope signatures of gas measured in shallow (<158 m) core samples from five scientific core drillings in southern Sweden, viz. Albjära-1, Lönstorp-1, Gislövshammar-2, Hällekis-1 and Djupvik-1 (Fig. 1, Table 1). Sampling and analyses were performed in 1991–1992 as part of the *Energy Research Project EFP-1313/88-2* and the *Pre-Westphalian Source-Rocks in Northwest Europe* (PREWSOR) project (Schovsbo & Laier 2012). This paper aims at further characterising the gas composition.

Samples and analyses

The molecular composition and isotope signatures of the occurring gases were measured in 27 core samples (Table 1). The samples were selected during drilling and consist of 4–8 cm long core intervals with a diameter of 5.5 cm. The samples from Albjära-1 and Lönstorp-1 were sealed in metal containers and stored at –18°C until they reached the laboratory for analysis. The free gas was subsequently ana-

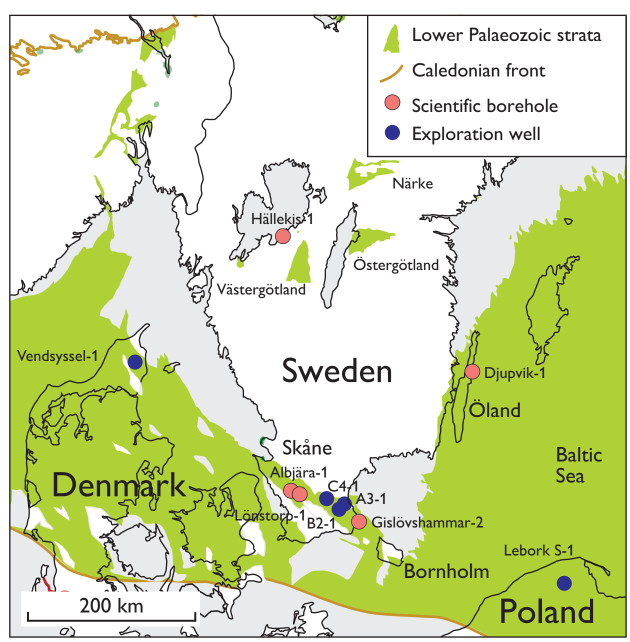


Fig. 1: Location of wells mentioned and occurrence of Lower Palaeozoic strata in southern Scandinavia. Modified from Nielsen & Schovsbo (2015).

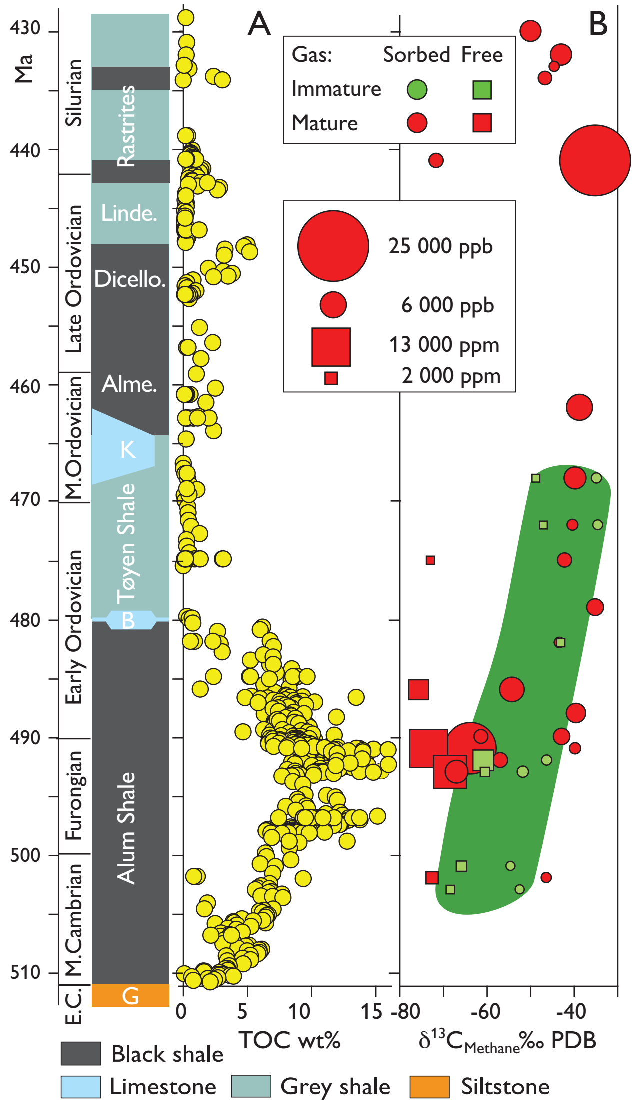


Fig. 2. Stratigraphy of the Lower Palaeozoic shales. **A**: Total organic carbon (TOC) content in shales from the Skåne–Bornholm area (modified from Schovsbo 2003). **B**: Methane isotope composition of sorbed and free gas from samples of thermally mature shale in the Albjära-1, Gislövshammar-2, and Lönstorp-1 wells and from samples of thermally immature shale in the Hällekis-1 and Djupvik-1 wells. **E.C.**: Early Cambrian. **G**: Gislöv Fm. **B**: Bjørkåsholmen Fm. **K**: Komstad Limestone. Alme.: Almelund Shale. Dicello.: Dicellograptus shale. Linde.: Lindegård Formation. Green area in **B** outlines the variation field defined by samples from the Djupvik-1 and Hällekis-1 wells.

lysed by the Geological Survey of Denmark and Greenland (GEUS) by puncturing the containers through a septum before opening. Samples from Gislövshammar-2, Hällekis-1 and Djupvik-1 were analysed by the Federal Institute for Geosciences and Natural Resources (BGR), Germany. These samples were stored at –18°C at the drill site and

Table 1. Wells and analysed samples§

Well	Formation	N	Depth range (m)
Gislövshammar-2	Tøyen S.	1	19.8
Gislövshammar-2	Alum S.	4	31.8–88.3
Djupvik-1	Alum S:	1	2.0
Hällekis-1	Tøyen S.	2	9.9–17.3
Hällekis-1	Alum S,	4	23.4–39.8
Albjära-1	Almelund	1	99.6
Albjära-1	Tøyen S.	3	114.8–134.5
Albjära-1	Alum S.	5	139.6–157.0

§Full analytical results are available on request from the first author.

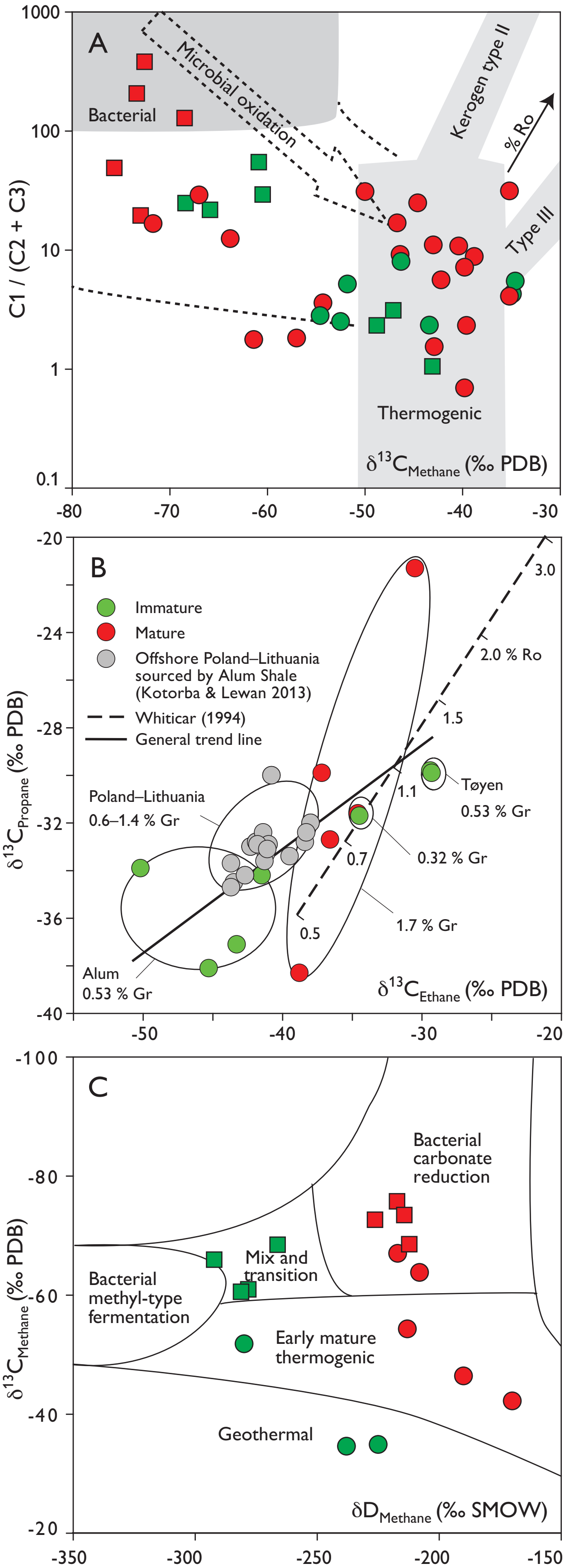
subsequently transferred to a container filled with liquid nitrogen at –196°C. The free gas was measured by allowing the deep-frozen sample to equilibrate to room temperature in a sealed container. For all samples the sorbed gas in the rock matrix was liberated by treating the sample with phosphoric acid following the procedure outlined by Faber & Stahl (1983).

Gas composition

The sorbed methane concentrations range from 118 to 23867 ppb (micrograms per kg of rock) and the free gas contents from 3 to 13420 ppm (Fig. 2). The concentrations thus far exceed the level of background gas of 20–50 ppb for methane as defined by Whiticar (1994). The gas content is strongly related to thermal rank of the sampled shales. The gas-mature samples from Gislövshammar-2, Albjära-1 and Lönstorp-1 have *c.* ten times higher yields than the thermally immature samples from the Hällekis-1 and Djupvik-1 wells (Fig. 2). The gas content appears not to be related to the total organic content in the mature samples. This is exemplified by the fact that the highest yields of sorbed gas are found in the Rastrites Shale (TOC average <1%) and the lowest yields in the Alum Shale, which on average contains 9% TOC in Skåne and on Bornholm (Fig. 2).

Isotope composition and carbon isotope signatures

The gas molecule and isotopic compositions of the analysed samples plot within the bacterial to thermogenic fields in a Bernard diagram (Fig. 3A). The microbial gas is characterised by much higher negative isotope values than seen in the thermogenic-sourced methane. This signature is most clearly expressed in the free gas samples from mature shales that also have 10 to 100 times higher $C_1/(C_2+C_3)$ molecular ratios than the sorbed gas, which is also typical for biogenic gas (Fig. 3A).



The propane versus ethane isotope gas signature is suggested to reflect the maturity of the source and this relationship can be used for a gas-to-source-rock correlation (Whiticar 1994). The analysed gas signatures follow this prediction, as immature Alum Shale samples from the Hällekis-1 well plot with relatively depleted isotope signatures of propane and ethane compared to the thermally mature Alum Shale samples (Fig. 3B). Isotope data from Lithuanian and Polish oil and gas reservoirs in Middle Cambrian sandstone, sourced by Alum Shale (Kotarba & Lewan 2013), plot with intermediate signatures (Fig. 3B).

The thermally mature samples (Gislövshammar-2 well), however, exhibit a considerable variation in propane isotope composition from –22 to –39‰ PDB, suggesting a mixture of differently derived gases. This may be caused by addition of bacterially derived ethane and/or biodegradation of a propane component (cf. Whiticar 1994). The thermally immature Alum Shale samples from the Djupvik-1 well (marked with 0.32 %Gr in Fig. 3B) and samples from Tøyen Shale from the Hällekis-1 well (marked as Tøyen 0.53%Gr in Fig. 3B) plot within an apparent gas maturity of 0.8–1.2% Ro according to the values indicated in Fig. 3B (Whiticar trend line), i.e. with much higher maturities than measured, suggesting that gas migration has occurred. In the Hällekis-1 well the migrated gas may have formed in response to intrusion of Permo-Carboniferous dikes that locally matured the shales in south central Sweden (cf. Schultz *et al.* 2015). In the vicinity of the Djupvik-1 drill site-mature shale and igneous activity are unknown and the relatively high maturity remains puzzling.

Deuterium isotopes

Measurements of deuterium and carbon isotopes in methane offer additional information on the source of the natural gases and on the processes that may have modified their composition (Whiticar 1994). Figure 3C shows the deuterium versus carbon isotope composition of methane in the analysed samples. The gas composition exhibits a

Fig. 3. Compostion and isotope signatures of organic carbon. **A**: 'Bernard diagram' showing the ratio $C_1/(C_2+C_3)$ versus $\delta^{13}C_{Methane}$ for all samples. This type of diagram is used to determine the origin of the gases and is modified from Whiticar (1994). For legend, see Fig. 2. **B**: Relationship between $\delta^{13}C_{Ethane}$ and $\delta^{13}C_{Propane}$. Tøyen and Alum 0.53% Gr denote stratigraphy and maturity of samples from the Hällekis-1 well. The graptolite reflectance (% Gr) is from Pedersen *et al.* (2013); Grönvik locality is used for Djupvik-1; estimate for offshore Poland. **C**: δD and $\delta^{13}C$ for methane. For legend, see Fig. 2. The isotope signatures of the various sources are from Whiticar (1994).

large degree of scatter, but free gas from thermally mature samples plots in the bacterial carbonate reduction field, whereas free gas from immature samples plots towards the bacterial methyl-type fermentation fields, suggesting that different processes generated the depleted methane isotope compositions (Fig. 3C). The sorbed gas compositions in general plot away from bacterial sources, indicating that a thermogenic signature is preserved (Fig. 3C).

Implications for shale-gas prospectivity

The gas-isotope composition suggests that significant post-generation modification occurred although the timing is unknown. The biogenic isotope signature of the gases in Skåne resembles similar signatures seen in Östergötland (Schultz *et al.* 2015). Here Schultz *et al.* inferred that methyl-fermenting processes contributed to the methane content. However, the gas-isotope signature was not as depleted as seen in this study, possibly owing to the mixed shale oil – biogenic nature of the Östergötland Alum Shale play. According to Schultz *et al.* (2015) the biogenic gas was generated after the Pleistocene glaciation, as modern meteoric water was able to infiltrate the shale and create the right conditions for bacterial activities. We envisage that similar conditions may have affected the shallowly buried shales in Skåne. Krüger *et al.* (2014), however, show that highly mature kerogen has a much smaller microbial generative gas potential than immature to marginally mature kerogen, since thermal maturity limits the amount of easily biodegradable organic matter that can be transformed to methane.

Conclusions

Lower Palaeozoic shales in south central Sweden and southernmost Sweden contain natural gas that exceeds the level of background gas. The gas content is strongly related to the thermal rank of the sampled shales, and mature samples have approximately ten times higher yields than the immature samples. The gas is generated by both thermogenic and bacterial processes. The microbial gas signature is most clearly expressed in the free gas samples from mature shales that also have 10 to 100 times higher molecule $C_1/(C_2+C_3)$ ratios than the sorbed gas. Migration may have occurred related to gas formation in response to intrusion of Permo-Carboniferous dikes that locally matured the shales in south central Sweden.

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